

**PIDDP FY00 PROPOSAL FINAL REPORT**

"Atmospheric Trace Gas Abundances & Stable Isotope Ratios via IR-LIF (NAG5-9471)"

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**ORIGINAL PROPOSAL ABSTRACT.** We propose to develop new technologies with support provided by PIDDP that will enable the in situ measurements of abundances and stable isotope ratios in important radiatively and biogenically active gases such as carbon dioxide, carbon monoxide, water, methane, nitrous oxide, and hydrogen sulfide to very high precision (0.1 per mil or better for the isotopic ratios, for example). Such measurements, impossible at present, could provide pivotal new constraints on the global (bio)geochemical budgets of these critical species, and could also be used to examine the dynamics of atmospheric transport on Mars, Titan, and other solar system bodies. We believe the combination of solid state light sources with imaging of the IR laser induced fluorescence (IR-LIF) via newly available detector arrays will make such in situ measurements possible for the first time. Even under ambient terrestrial conditions, the LIF yield from vibrational excitation of species such as water and carbon dioxide should produce emission measures well in excess of ten billion photons/sec from samples volumes of order 1 c.c. These count rates can, in principle, yield detection limits into the sub-ppt range that are required for the in situ isotopic study of atmospheric trace gases. While promising, such technologies are relatively immature, but developing rapidly, and there are a great many uncertainties regarding their applicability to in situ IR-LIF planetary studies. We therefore feel PIDDP support will be critical to developing these new tools, and propose a three-year program to combine microchip near-IR lasers with low background detection axes and state-of-the-art HgCdTe detectors developed for astronomical spectroscopy to investigate the sensitivity of IR-LIF under realistic planetary conditions, to optimize the optical pumping and filtering schemes for important species, and to apply the spectrometer to the non-destructive measurement of stable isotopes in a variety of test samples. These studies form the necessary precursors to the development of compact, lightweight stable isotope/trace gas sensors for future planetary missions.

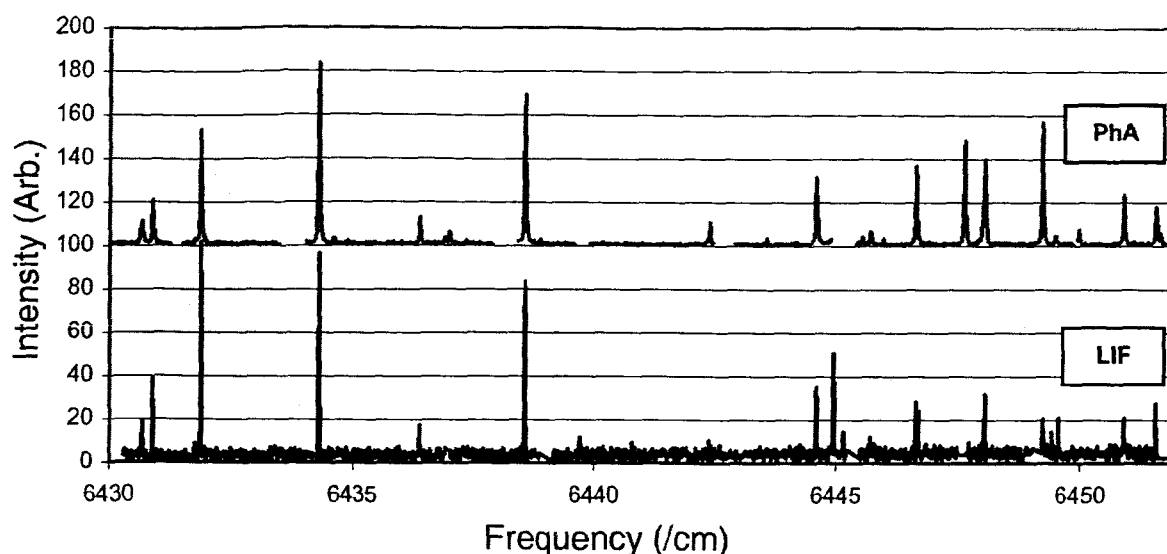
## Final Report for NAG5-9471

As described in the original proposal, research in the Blake group supported by the NASA Planetary Instrument Definition and Development Program (PIDDP) program sought to develop a new class of ultra-lightweight laser-based instrumentation for the measurement of the abundances and stable isotope ratios of trace atmospheric gases. The spectroscopic modes used for this work are molecular vibrations, and so the transitions of interest occur in the near- to mid-infrared (near- to mid-IR). Most studies at these wavelengths are based on long pathlength absorption spectroscopy using continuous wave (cw) diode lasers. In such an approach, the absorption is measured by comparing the instrument transmission as a function of the laser wavelength as it is scanned, and as a result even small fluctuations in the large carrier signal can lead to systematic errors in the abundance or isotope ratio measurements. The complex geometry of the multi-pass cell also leads to larger instrument size, although the weight penalties are now rather minor with modern designs and honeycombed materials.

In contrast, our approach uses infrared laser induced fluorescence (IR-LIF) to carry out the measurements of interest. Like the absorption technique, the ultimate implementation of IR-LIF will utilize diode lasers to excite the vibration of interest. In the laboratory set up used by the group we employ both diode lasers and non-linear optical methods, in particular those based on optical parametric oscillators, or OPOs, to generate light at the appropriate wavelengths. For the initial survey work that determined the best excitation wavelengths, the OPOs combine the advantages of good line width control with exceptionally broad tunability. A single optical cavity has been used during this proposal period to excite molecules as diverse as CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>, HCN, and NH<sub>3</sub> along with their isotopologues. With diode lasers, many devices would be required and even then complete spectroscopic coverage of the relevant vibrations would not be guaranteed.

After excitation, the resulting IR fluorescence is monitored. Like a mass spectrometer, the idea is to create an instrument in which the signal itself dominates the systematics, and in which the ultimate S/N and precision is dominated by shot noise in the information carriers (photons in this case, ions in the case of mass spectrometry). Further, the spectroscopic nature of the technique makes it possible to distinguish between nominally isobaric species such as <sup>13</sup>CO<sub>2</sub> and OC<sup>18</sup>O or <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O and <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O without any processing of the sample.

The research proposed in our original application to PIDDP had two major components: (1) The characterization, in the laboratory, of the optimum laser excitation and LIF detection wavelengths using our existing OPO and diode laser light sources and a HgCdTe array-based grating spectrometer to be built in collaboration with Boeing North American, and (2) The fabrication of a simple prototype instrument for one species (given the focus on Mars either CO<sub>2</sub> or H<sub>2</sub>O) using either quantum cascade lasers or commercially available telecommunications lasers in the near-IR. In the proposal, the second component was to be carried out in year three at Caltech after the laboratory characterizations are complete for the species of interest. Thanks to additional support from the PIDDP program to the Jet Propulsion Laboratory, the first stages of the prototyping effort were in fact carried out jointly with Dr. Pin Chen, a member of Dr. Chris Webster's group at JPL. The Webster group is well known for their pioneering development of autonomous diode



**Figure 1.** Photoacoustic cell (top) and IR-LIF (bottom) spectra of the HDO  $\nu_1 + \nu_3$  combination band near  $1.55 \mu\text{m}$ . The photoacoustic cell spectra used a 50:50 mix of  $\text{D}_2\text{O}:\text{H}_2\text{O}$ , while the LIF spectra were taken with ratios only a few times SMOW (Standard Mean Ocean Water) that are a good approximation of the current Martian atmosphere.

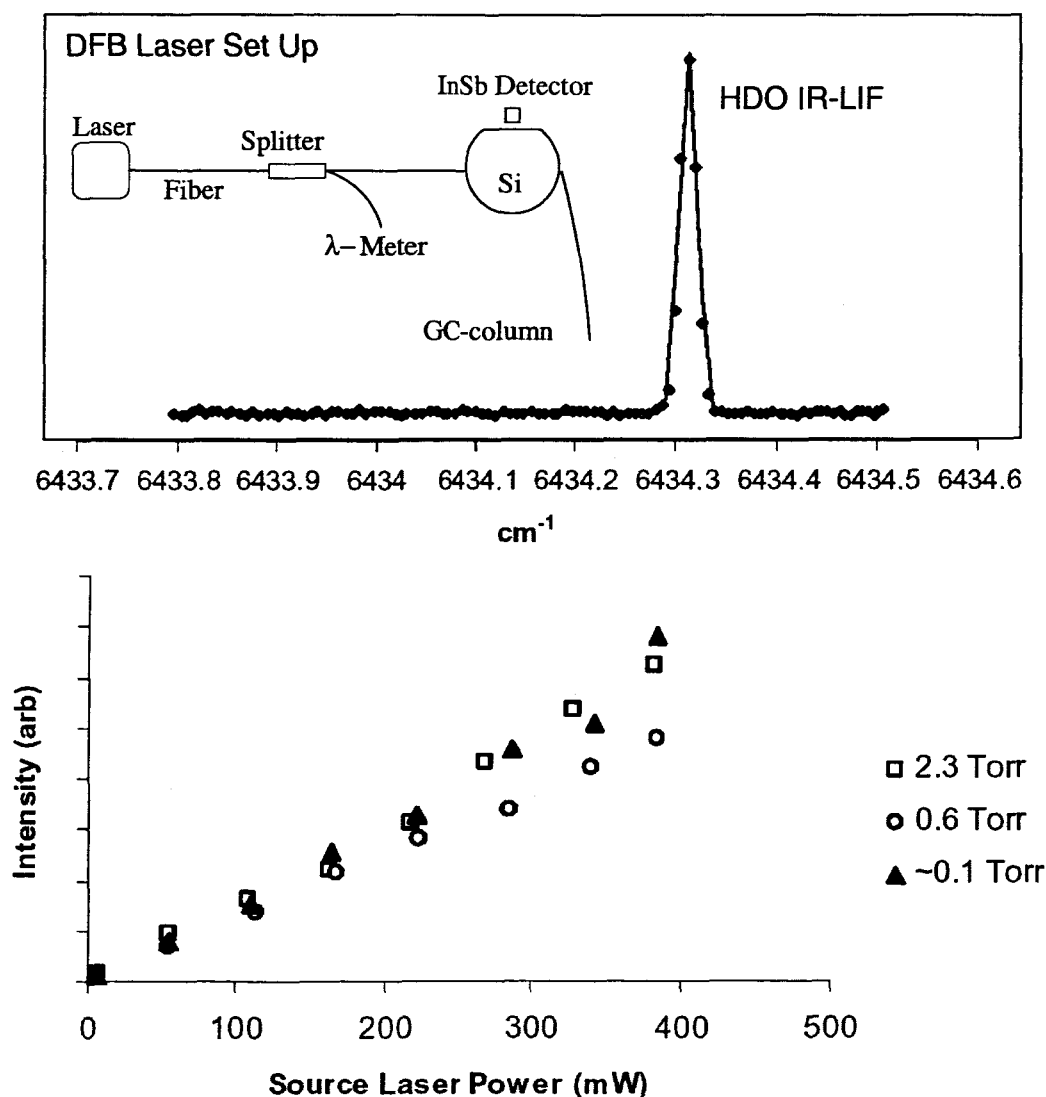
laser based *in situ* spectrometers, and as described below this collaboration has enabled a much more aggressive use of state-of-the-art technology that has already made its way into the space exploration program.

Thanks to their importance in paleoclimate and exobiology, our primary targets have been the isotopes of water and  $\text{CO}_2$ , using near-IR overtone and combination bands. We had originally used our OPO light sources and a simple liquid helium cooled InSb detector array on loan from our colleagues in infrared astronomy, but have found that the sensitivity of IR-LIF for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is potentially much better if continuous wave lasers developed for the telecommunications industry are used since the “repetition rate” in this case is defined by the collisional relaxation time scale and not the pulse rate of the laser. Our laboratory IR-LIF tests have yielded a number of interesting results, particularly for the (P,T) regime expected for experiments on the Martian surface. As expected, when moving to overtone or combination band pumping, the rejection of the prompt laser (or Rayleigh) scatter is dramatically enhanced since the excitation and detection wavelengths are dramatically different.

Figure 1 presents an overview of the sensitivity achieved with such a simple system for HDO. The volume imaged by the LIF setup corresponds to only a few hundred  $\mu\text{m}^3$ , and so the sample required to generate such signals is only of order 1 picomole. Such small volumes enable novel sampling geometries and spectrometer miniaturization efforts to proceed. Figure 2, for example, presents spectra of the strong HDO transition near  $6434.3 \text{ cm}^{-1}$  with a dedicated, fiber-coupled DFB laser and Er-amplifier system. The laser radiation propagates through polarization-maintaining fiber up to a hollow dielectric waveguide micromachined in high purity silicon. The other end of the waveguide is attached to a standard high pressure gas chromatography column in order to deliver sample.

The high purity Si is transparent to  $\lambda > 7\mu\text{m}$ , and can easily be coated for high reflectivity or transmission. Thus, it serves as an excellent miniature sample holder to which cooled detector housings can be attached. Figure 2 shows the HDO spectrum obtained with a first version of this set up, as can be seen the SNR is excellent.

Interestingly, the lifetimes of the vibrational states such as that pumped here in HDO are long compared to the collision time scales of typical planetary atmospheres. The IR fluorescence yield is therefore dependent upon the pressure of the sample. For molecules with constant mixing ratios with altitude, the increase in collisional decay balances the increasing concentration, and the sensitivity is largely independent of altitude (or pressure, though the technique is temperature sensitive, as is absorption spectroscopy) – provided sufficient laser power is available (more below). This unique attribute of IR-LIF is demonstrated in the lower panel of Figure 2.



**Figures 2.** DFB laser IR-LIF spectrum of the isolated HDO  $2_{11} \rightarrow 2_{02}$  transition (top), and a power versus signal plot for three different sample total pressures (bottom).

The other interesting aspect of Figure 2 is the power dependence of the IR-LIF signal – it is linear to several hundred mW of average power in spot sizes of only a few hundred square microns. This corresponds to power densities of nearly a kW/cm<sup>2</sup>, much more than is needed to saturate the rovibronic transition under collision free conditions! The key here is the fast relaxation provided by translation-rotation energy transfer. Effectively, these collisions rapidly populate the entire  $\nu_1 + \nu_3$  rotational manifold, which becomes free to decay by emission or through vibrational quenching collisions (T-R transfer is much faster than T-V transfer) independent of the laser radiation field. This has important implications for the high dynamic range measurement of isotopic ratios. For D/H in water, for example, we have set up two DFB lasers at 1370.0 nm (for H<sub>2</sub>O) and 1554.2 nm (for HDO), which drive fluorescence that can be detected by the same InSb element and filter combination. The power ratio is set up such that roughly equal count rates are obtained, dramatically improving the signal-to-noise such that stable isotope mass spectrometer-like performance has been obtained in a compact laboratory instrument.

For species other than water, the IR-LIF occurs at rather longer wavelengths; and in order to optimize the experimental sensitivity, it is necessary to reduce the background to as low a level as possible. We have therefore assembled a simple, quantitatively calibrated flow system that houses a L<sub>N<sub>2</sub></sub> cooled low emission/background fluorescence chamber. The static sample volume needed is only of order 1 mm<sup>3</sup>, and the background is fully ten-twenty times lower than that of a room temperature system at 4.5  $\mu$ m. Indeed, for the studies involving the combination bands of water and HDO our background is sufficiently low that the major source of “noise” is Raman scattering from the target molecule of interest.

Our initial experiments outlined in Figures 1 and 2 were conducted using the first overtone bands or combination bands in which the vibrational mode involved in the fluorescence is combined with at most one quantum from another mode. We have found, as was known for simpler molecules from chemical laser energy transfer studies, that the vibrational quenching rate rises roughly linearly with the vibrational quantum number (unless states that have accidental near degeneracies are pumped). The Einstein A-coefficients also rise roughly linearly with vibrational quantum number, and the rise in collisional quenching is largely mitigated by the improved fluorescence yield. What is very dramatic about pumping these higher energy modes is the huge drop in Raman cross sections – nearly a factor of one hundred for the molecules of interest. Thus, the emission rates are similar but the major source of background noise has been reduced enormously.

We have therefore achieved the most important goal of the original PIDDP proposal – we have demonstrated that extremely high precision stable isotope measurements can be obtained under planetary atmospheric conditions with lasers that are entirely compatible with present spacecraft technology. What are the next steps?

As outlined above, to take maximum advantage of the properties of IR-LIF for stable isotope measurements, it is desirable to achieve power density levels near 0.1-1 kW/cm<sup>2</sup> in volumes of a few hundred cubic microns since the emission rates scale directly with power for all conceivable missions to Mars or satellites such as Titan. In the laboratory this is straightforward to achieve with optical amplifiers, but this approach has issues in terms of the lander power requirements needed (size and weight can be reasonably well accommodated) for *in situ* applications.

For these reasons, we are continuing to work extensively on the construction and optimization of a prototype miniaturized stable isotope ratio spectrometer with Dr. Pin Chen and the Webster group at JPL. Over the past year this joint JPL/Caltech effort was funded, in part, by the Astrobiology Science and Technology Instrument Development Program. In particular, we have worked toward setting up a *combined* long pathlength absorption and IR-LIF experiment, in which the multi-pass cell needed for the absorption work serves to enhance the laser power density to levels that optimize the IR-LIF measurements. The ASTID program funded the development of the hybrid cell and the control electronics for the miniaturized spectrometer, the PIDDP funds were used to construct the IR-LIF axis and pay for the Caltech personnel associated with this effort.

The idea of this miniaturized joint instrument is to provide *simultaneous* absorption and emission measurements in the field, with the absorption measurements on the abundant parent species serving to accurately calibrate the IR-LIF detection system. Absorption measurements can be very well calibrated, but suffer from poor systematics for very weak absorptions. The IR-LIF technique has extremely high sensitivity, but is more difficult to calibrate since the absolute signal for a given species is pressure independent! By using the long pathlength cell to measure the concentrations of species such as  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , the IR-LIF signals from these species can be very accurately calibrated and the isotope ratios extracted from the fluorescence signals of the less abundant isotopologues. The necessary drive electronics for the diode lasers, including that necessary to drive the revolutionary new quantum cascade laser technology, already exist in the Webster group. Space qualified versions of the necessary lasers, electronics, and cell technology have already been developed for the Mars Polar Lander. Thus, an important aspect of this collaboration is the rapid time scale over which IR-LIF can be brought into readiness for flight opportunities.

For a true field instrument, background from solar scatter or dust will need to be considered, and cryogenics are not appropriate. Fortunately, the low temperature imaging backstop can be powered by the same high efficiency Stirling cooler that would be needed to operate the detectors – no cryogenics will be required in the final design. In some planetary exploration cases Raman scattering from nitrogen is large, and this would be an issue for experiments at Titan. This signal can be mitigated by careful choice of the excitation wavelength, however, and can be easily evaluated using the tunability of the OPOs. We therefore plan to redesign our existing cryogenic detection axis to provide better shielding against the sun while retaining high throughput of the desired signal. This design work will be carried out with Prof. Paul Wennberg and his group at Caltech, who have extensive experience with the design, construction, and operation of high sensitivity airborne spectrometers for OH and other reactive intermediates.